

PATENT SPECIFICATION

23 APR. 1980

(11) 1 564 801

1 564 801

- (21) Application No. 46217/75 (22) Filed 7 Nov. 1975
 (23) Complete Specification filed 5 Nov. 1976
 (44) Complete Specification published 16 April 1980
 (51) INT CL³ A23D 3/00
 (52) Index at acceptance
 C5C 9B3 9B4 9B6 9B7 9B8 9B9CX 9BX 9EX



(54) PHASE INVERTING LOW FAT SPREADS

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E/C 4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to water-in-oil type low fat spreads.

A problem that is often encountered in emulsions of water-in-oil type in low fat spreads is that an insufficient flavour-release takes place by chewing the product in the mouth, because a substantial proportion of water droplets — which contain flavouring material e.g. salt — do not reach the papillae in the mouth but remain enveloped with the continuous fat phase.

An improvement in flavour release can in principle be achieved by taking care that the product has a coarser emulsion structure than conventional products, so as to obtain a more unstable emulsion, which upon mastication on the palate will give a better flavour release. From a micro-biological point of view, however, such emulsions are dangerous, since water separation can easily take place merely upon storage which may result in unacceptable bacteriological infections of the product.

The present invention provides an emulsion particularly for use in low fat edible spreads, which comprises 50—65% by weight of a dispersed aqueous phase of a pH value of 4—6 and 50—35% by weight of a continuous fat phase containing a minor amount of a partial glyceride emulsifier, the fat having a solid content of 10—35% at all temperatures from 10—20°C, a difference in solid content at 10° and 20°C of no more than 10%, and a solid content at 30°C of less than 5%, and preferably of no more than 0.5, especially no more than 0.1% at 35°C, the emulsion having a phase instability temperature of 10—40°C, preferably at least 15°C, particularly from 20—35°C.

In this specification by "phase instability temperature" (PIT) is understood the temperature at which the emulsion, under shear conditions similar to those that occur on the palate and as measured by the "PIT-test," which will hereinafter be described, shows a marked increased tendency to conduct electricity.

The terms "dispersed phase" and "continuous phase" refer to the condition of the emulsion at room temperature, i.e. about 20°C.

In this specification all percentages are by weight and are calculated on the total weight of the low fat spread (except the solid contents) unless otherwise indicated. The solids contents are expressed as percentages by weight and are calculated on the weight of the fat blend. The solids contents were measured by the method of Haighton, Vermaas and Den Hollander as described in J.A.O.C.S. Vol. 48, pages 7—10.

An advantage of the low fat spread of the invention is that a substantial proportion of the dispersed aqueous phase is released in the mouth, whereby water-soluble emulsifiers are freed into the saliva, which causes the former fat-continuous phase to emulsify into the saliva, thereby giving an oil-in-water emulsion in the mouth. In the low fat spread of the invention up to 90% or even more of the dispersed aqueous phase can break out under palate conditions within about 10 seconds. This will result in a rapid flavour release, not only because the water-soluble flavours are released, but also because of a rapid partition of essentially oil-soluble flavour components into the saliva, which become part of the continuous aqueous phase under palate conditions, due to the high interfacial area of the oil-in-water emulsion which is formed.

The dilatometric characteristics of the fat blend of the emulsion of the invention will substantially avoid the formation of high-melting trisaturated triglycerides through recrystallisation on cycling of the temperature of the emulsion during storage,

which glycerides at relatively low levels would have under palate conditions W/O emulsion stabilizing properties.

5 The dilatometric characteristics of the fat blend also influence the product instability, especially under conditions of shear as met with on the palate. Preferably a fat blend is used having a solid content at 10°—20°C which is as invariable as possible, e.g. a difference in solid content between 10° and 10 20°C of no more than 5%. Products containing a fat blend of such a solids/temperature curve will have a minimum of melting and re-crystallisation of glycerides on cycling of the temperature 15 within the range of e.g. 10°—20°C, an improved feel of coolness on the palate during melting of the glycerides, and a low solids content at 30°C, which will help to avoid a greasy feel on the palate of the molten product. 20

The type and proportion of both the emulsifier system and the fat blend are of importance for ensuring a sufficient degree of product instability at palate conditions of shear. Suitable amounts of partial glycerides are from 0.1 to 0.8% by weight. Preferably partial glycerides are used that are not completely saturated, e.g. partial glycerides 25 of fatty acids with 16—22 carbon atoms and having an iodine value of 20—100, especially 30—60. 30

Monoglycerides of an iodine value of 30—60, especially 35—50, e.g. those of unhydrogenated lard or tallow are particularly preferred. The partial glycerides can be present in proportions within the range indicated above; preferably however the content of partial glycerides is adjusted to the fat content of the low fat spread of the invention. 35 40

Suitable weight ratios of fat: partial glycerides are e.g. from (50:1) to (500:1), preferably from (100:1) to (300:1). 45

Preferably the emulsion further comprises oil-in-water promoting emulsifiers, e.g. phosphatides, especially partly hydrolyzed phosphatides, and synthetic emulsifiers e.g. fatty acid sugar esters, polyoxyethylene sorbitan fatty acid esters known as Tweens, etc. e.g. in a proportion of 0.01, preferably 0.02 to 0.6% by weight. If phosphatides are used in the low fat spreads of the present invention, they preferably contain some 5—25% of mono-acyl glycerol phosphatides, particularly alpha-mono-acyl glycerol phosphatides, calculated on the total weight of phosphatides. Such phosphatides can be prepared by synthesis or by chemical hydrolysis (c.f. British Patent Application 18,163/68) or by enzymatic hydrolysis of diacyl glycerol phosphatides under conditions known per se (c.f. British Patent Specification 1,215,868). 50 55 60 65

Proteins can similarly be used as oil-in-water promoting emulsifiers.

Although no more than 0.01—0.6 per cent by weight thereof is sufficient for effecting phase inversion of the low fat spread under palate conditions, proportions up to 12%, preferably up to 8% can be used, since the excess proteins do not destabilize the emulsion under normal processing and storage conditions, provided that a suitable proportion of partial glycerides is present. Such oil-in-water promoting emulsifiers therefore assist in counterbalancing the water-in-oil promoting properties of the partial glycerides under palate conditions, without effecting destabilisation of the emulsion at normal storage, use and transport conditions. 70 75 80

Whole vegetable phosphatides, i.e. non-chemically treated or fractionated phosphatides derived e.g. from soya-bean, rapeseed or corn preferably need a more solid fat blend than emulsifiers of higher HLB values such as lysolecithin containing partially hydrolysed phosphatides, proteins etc. Such lower HLB emulsifiers probably need the grinding action of more solid fat crystals in the initial stage of mastication in order to promote the destabilisation of the low fat spread on the palate. 85 90 95

Suitably whole vegetable phosphatides are used in low fat spreads containing a fat blend having a solids content of 26—35% at 10°C and preferably 18—25% at 20°C.

Emulsifiers which like whole phosphatides are less efficient oil-in-water emulsifiers, i.e. those of HLB values of about 10—16, are preferably also used together with a fat blend of high solids content at 10° and 20°C. 100 105

Particularly proteinaceous water-soluble emulsifiers are preferred, since they are very potent counter-emulsifiers and furthermore they will protect the fat blend against oxidation. Finally such emulsifiers can contain natural flavours, e.g. those obtained through culturing. 110

When a fat blend of suitable solids content is used, the desired phase instability temperature can be obtained by properly balancing the following factors: 115

1. The nature and proportion of fat-soluble partial glyceride emulsifiers.

2. The nature and proportion of water-soluble emulsifiers. 120

Preferably the emulsion further comprises hydrocolloids in the aqueous phase for raising the interfacial stability and also enhancing the emulsion-stabilising properties of the fat crystals under use and storage conditions. The concentration of hydrocolloids should be chosen in such a way that a proper balance in viscosity of the continuous fat phase and the dispersed aqueous phase is obtained. A suitable 125 130

hydrocolloid content can vary from 0.1 to 1.5% by weight.

Further advantages of using hydrocolloids, particularly locust bean gum, are its hardness-decreasing influence on the plastic emulsions of the invention and it also helps to control the palate sensation of the released aqueous phase in terms of viscosity.

It has surprisingly been observed that locust bean gum and milk proteins have a synergistic effect on the increase of viscosity.

PIT-Test

A Haake Rotovisko is equipped with the MV measuring system. The Haake MVII bob is used at speed 1, under which conditions the shear rate being applied to the sample is 441 sec^{-1} , which is a high but representative figure for the conditions on the palate.

Electrodes, made from aluminium foil, are inserted between the MVII bob and the Haake measuring cup wall. (The electrodes are 1 cm. wide and 15 cm. long). Those parts of the electrodes which can come into contact with the cup wall were insulated with a layer of glue of the trade name "Araldite."

The electrodes are connected to a conductivity bridge, for measuring the conductivity of the emulsion under test.

Measurements of conductivity and viscosity are made at 5°C intervals starting e.g. from 20° or lower to the PIT, which is the temperature at which conductance increases markedly, i.e. with at least 10^4 micro-Mhos, or to 70°C if no inversion (thus no marked increase in conductivity) can be detected. The emulsion is maintained at each temperature for 15 minutes, to ensure that equilibrium has been reached and the Rotovisko bob is kept rotating at speed 1 throughout the experiment.

The invention will now be illustrated by

the following examples in which all proportions and percentages are by weight and are calculated on the weight of the low fat spread, unless otherwise indicated.

Example I

A fat phase consisting of palm oil mid-fraction (30 parts) and sunflower oil (70 parts) was prepared, refined and deoderised. The solid content of this blend was: at 10°C 24%, at 20°C 17%, at 30°C 2% and at 35°C 0%. The palm mid-fraction was obtained by acetone fractionation of palm oil as follows:

(a) 300 g. of refined deoderised palm oil of I.V. 53.4 were mixed with $1\frac{1}{2}$ litres of acetone and the mixture warmed until a clear solution was obtained (30°C). The solution was then cooled to 6.5°C over $\frac{1}{2}$ hour whilst being gently stirred with a glass rod. It was allowed to stand for $\frac{1}{2}$ hour at 6.5°C and then filtered through a cooled Buchner funnel with vacuum. The cake was pressed with a glass plunger, and then washed twice on the filter with 250 ml. acetone at 5°C , for each wash, the cake being pressed between each wash. It was then removed from the filter and the residual acetone distilled off under vacuum. The yield was 93.9 g. of a fraction having an I.V. of 28.9.

(b) To 80 g. of the product of stage (a) were added 80 ml. of acetone and the mixture warmed to 45°C . To this were added 400 ml. of acetone at 19°C with stirring and the final temperature of the mixture adjusted to 26°C . It was allowed to stand at this temperature for 20 minutes and then filtered through a Buchner funnel, pressed and washed on the filter with 250 ml. acetone at 26°C . The filtrate and wash liquor were combined and the acetone removed by distillation under vacuum. The yield was 67.5 g. Its characteristics are given in the following table:

Component/ characteristics	Palm Mid-Fraction
Iodine value	34.4
Melting point (°C)	33.4
Refractionation index N _D ⁶⁵ 1.4	468
f.f.a. (%)	0.1
Monoglycerides (%)	traces
Diglycerides (%)	1.5
Triglycerides * (%)	98.5
S ₃ (% of triglycerides)	3.1
S ₂ U (% of triglycerides)	83.6
SU ₂ (% of triglycerides)	9.8
U ₃ (% of triglycerides)	3.5
Fatty acid composition **	
C 14 : 0	0.4
C 16 : 0	57.1
C 16 : 1	
C 17 : 0	
C 18 : 0	7.5
C 18 : 1	32.0
C 18 : 2	3.0
C 20 : 0	traces
C 20 : 1	

* S = saturated ; U = unsaturated.

** e.g. C 18 : 1 = mono-unsaturated C₁₈ fatty acid.

5 A low fat, water-in-oil spread product was prepared containing 39.8% of the palm mid/sunflower oil blend, melted under nitrogen at 40°C and 0.2% of commercial monoglyceride of unhydrogenated lard of an iodine value of 44 dissolved in the blend, the percentages being by weight of the product in this and the following examples, except where otherwise stated.

To the above mixture oil-soluble flavours and colour were also added.

The water phase of the product was prepared by dissolving 1.75% sodium chloride in 58.25% water.

0.05% of a water-soluble lecithin fraction, obtained through partial hydrolysis with phospholipase A of soyabean phosphatides as described in British Patent Specification

15

1,215,868 was then dispersed in the water phase. (The content of alpha-mono-acyl glycerophosphatides was about 12% of the total phosphatide content.)

- 5 A viscosity raising agent was added to the water phase, i.e. 0.75% locust bean gum.

The pH of the water phase was adjusted to a value of 4.5 to 5.5 by citric acid.

- 10 An emulsion of the aqueous phase in the fat phase was prepared by slowly adding the water phase to the fat phase, with gentle stirring, at 35°C.

- 15 The emulsion formed was then processed through a conventional Votator, consisting of two A-units (scraped surface coolers) in which the product was worked and cooled to 15–20°C, and one P.C.U. (post-crystallizing unit) to provide a low fat spread. "Votator" is a Registered Trade Mark.

Example II

- 25 A fat phase consisting of 32.15% soyabean oil (hardened to m.pt. 35°C), 21.53% partially hardened rapeseed oil, 9.32% soyabean oil (hardened to m.pt. 42°C) and 37.0% sunflower oil, was refined and deoderised (% calculated on the weight of the fat blend).

- 30 The solid content of this blend was: at 10°C 32%, at 20°C 24%, at 30°C 2.5% and at 35°C 0%.

- 35 A low fat, water-in-oil spread product was prepared containing 39.7% of the above blend, melted under nitrogen at 40°C, into which 0.3% of commercial monoglycerides of unhydrogenated lard of an iodine value of 44 was dissolved.

- 40 To the above mixture oil-soluble flavours were added.

- 45 The water phase of the product was prepared by dissolving 0.5% buttermilk powder in 53.8% water.

- 50 The buttermilk solution was heated to 95°C and into this 1.75% salt, 0.1% sodium tripolyphosphate, 0.1% potassium sorbate and 0.75% locust bean gum were dissolved.

- 55 The solution was cooled to 45°C and 3% cultured buttermilk was added.

- 60 The pH of the mixture was adjusted to 4.5 to 5.0 with tartaric acid.

An emulsion of the aqueous phase in the fat phase was prepared by slowly adding the aqueous phase to the oil with gentle stirring.

- The emulsion was then processed through a conventional Votator system consisting of an A-unit (scraped surface cooler) and a P.C.U. (post-crystallising unit).

- The low fat spread product was packed into tubs at 15°C.

- 60 The PIT was about 20°C.

Example III

A fat phase consisting of palm oil mid-fraction (25%) with sunflower oil (75%) was

prepared, refined and deoderised. The palm oil mid-fraction was prepared as described in Example I. The solid content of the fat blend as at 10°C 19%, at 20°C 12%, at 30°C 1%, at 35°C 0%.

A product was prepared as before, comprising 39.7% of the palm mid/sunflower oil blend melted at 40°C, into which 0.2% of commercial monoglyceride of unhydrogenated lard with an iodine value of 44 and 0.1% whole soyabean phosphatides were dissolved.

The water phase of the product was then prepared by dissolving 1.75% sodium chloride in 58.25% water.

The pH of the water phase was adjusted to a pH of 4.5 to 5.5, using citric acid.

An emulsion of the aqueous phase in the fat phase was prepared by slowly adding the water phase to the fat phase with gentle stirring at 35°C.

The emulsion was then processed through a conventional Votator, consisting of two A-units (scraped surface coolers) and one P.C.U. (post-crystalliser working unit).

The product was packed at 10–15°C into tubs.

The amount of aqueous phase released under simulated palate conditions (440 secs⁻¹, 37°C, 10 secs) was 70%.

The PIT was about 26°C.

Example IV

A product was prepared as described in Example III, using the same fat phase.

38% of the palm mid/sunflower oil blend was melted under nitrogen at 45°C and into this 0.5% of commercial monoglyceride of unhydrogenated lard of an iodine value of 44 was dissolved.

56.7% of water was heated to 95°C and into this 1.0% of salt and 0.75% of locust bean gum was dissolved using vigorous stirring to ensure complete solution of the gelling agent.

The mixture obtained was cooled to 45°C, and 3% cultured buttermilk was added to the mix.

The pH of the mix was adjusted to 4.5–5.0 with tartaric acid, an acid which allows a considerable drop in pH value without imparting too acid a taste to the product.

An emulsion of the aqueous phase in the fat phase was prepared by slowly adding the aqueous phase to the fat phase with gentle stirring at 45°C.

The emulsion was then processed through a conventional Votator consisting of an A-unit (scraped surface cooler) and a P.C.U. (post-crystalliser working unit).

The product was packed at 10–15°C into tubs.

The amount of aqueous phase released under simulated palate conditions (440

sec⁻¹, 37°C, 10 secs.) was 90%.

The PIT was: about 20°C.

Example V

- 5 A low fat spread was prepared as described in Example I using 59% of the same fat blend as was used in Example I and furthermore:

	monoglycerides from unhydrogenated lard (I.V. 44)	0.2%
10	water	32.4%
	sodium caseinate	6.2%
	salt	1.5%
	potassium sorbate	0.1%
	sodium tripolyphosphate	0.1%
15	locust bean gum	0.5%

The pH value was adjusted to 5.8 with citric acid.

The PIT was 20°C.

Example VI

- 20 Example I was repeated, except that the fat blend of Example II was used, that the partially hydrolysed phosphatides were replaced by whole soyabean phosphatides (0.05%) and that the monoglyceride content was raised to 0.3%.

- 25 The proportion of water was correspondingly adjusted.

The PIT was just over 30°C.

- 30 All the products of the above Examples provided a satisfactory taste response when tested, with good salt release in the mouth.

WHAT WE CLAIM IS:—

- 35 1. Emulsion comprising 50—65 per cent by weight of a dispersed aqueous phase of a pH value of 4—6 and 50—35 per cent by weight of a continuous fat phase containing a minor amount of partial glyceride emulsifier, the fat having a solids content of 10—35% at all temperatures from 40 10—20°C, a difference in solids content at 10 and 20°C of no more than 10% and a solids content at 30°C of less than 5%, the emulsion having a phase instability temperature, as hereinbefore defined, of 45 10—40°C.

2. Emulsion according to claim 1, in which the phase instability temperature is 20—35°C.

- 50 3. Emulsion according to claim 1 or 2, in which the solids content of the fat at 35°C is no more than 0.5%.

4. Emulsion according to any one of claims 1—3, in which the solids content of the fat at 35°C is no more than 0.1%.

5. Emulsion according to any one of claims 1—4, in which the difference in solids content between 10 and 20°C is no more than 5%.

6. Emulsion according to any one of claims 1—5, in which the partial glyceride content is from 0.1—0.8% by weight.

7. Emulsion according to claim 6, in which the partial glycerides are of fatty acids with 16—22 carbon atoms and have an iodine value of 20—100.

8. Emulsion according to claim 7, in which the iodine value is 30—60.

9. Emulsion according to any one of the preceding claims, in which the weight ratio of fat: partial glycerides is from (50:1) to (500:1).

10. Emulsion according to claim 9, in which the weight ratio is from (100:1) to (300:1).

11. Emulsion according to any one of claims 1—10, further comprising oil-in-water promoting emulsifiers.

12. Emulsion according to claim 7, in which the content of oil-in-water promoting emulsifiers is 0.02 to 0.6 per cent by weight.

13. Emulsion according to claim 11, in which the oil-in-water promoting emulsifiers are phosphatides.

14. Emulsion according to claim 13, in which the phosphatides contain 5—25% of monoacyl glycerophosphatides.

15. Emulsion according to claim 13, in which the phosphatides are whole vegetable phosphatides and that the emulsion contains a fat blend having a solids content of 26—35% at 10°C.

16. Emulsion according to claim 11, in which the oil-in-water promoting emulsifiers are proteins.

17. Emulsion according to claim 16, containing up to 12% of proteins.

18. Emulsion according to any one of claims 1—17, further comprising hydrocolloids in the aqueous phase.

19. Emulsion according to claim 18, in which the hydrocolloid content is from 0.1 to 1.5 per cent by weight.

20. Emulsion substantially as hereinbefore described with particular reference to any one of the examples I—VI.

21. Low fat water-in-oil spread comprising edible fat in an emulsion as claimed in any of the preceding claims containing flavouring material in the aqueous phase.

D. LITHERLAND
Chartered Patent Agent

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.